Indian J. Phys. **69A** (1), 133 – 139 (1995)

I J P A
— an international journal

An estimation of velocity correlation coefficients in ternary electrolytes

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Abstract: This work gives an estimate of the velocity correlation coefficients for ternary electrolyte solutions (the system may have tracer ion as any one of the component), originating from the linear response theory utilizing the measured transport coefficients in order to get a deeper insight into the microdynamic structure of the solution. Assuming Onsager's relation to be valid we obtain ten sets of velocity correlation coefficients for Cs ion transporting in aqueous solution of CsCl and KCl.

Key words: Velocity correlation coefficient, Ternary electrolyte, Diffusion Coefficient, Radioactive tracer.
PACS number: 66.0, 05.60

Introduction

The velocity correlation formalism evoked from the linear response theory is of great importance for envisaging the molecular motion and the particle-particle interaction in electrolyte solutions, specially in concentrated solutions (few tenth molar or higher than that) where Onsager's theory and its extensions fails to give real physical picture. Essentially the works of McCall and Douglass [1] and Douglass and Firsch [2] which showed first how mutual and self diffusion data can be interpreted in terms of integral over velocity self correlation functions and velocity cross correlation functions. Since then the field has been exercised with great ingenuity, but most

of these works deal with binary systems and even if with multicomponent systems no bridge was made to cover the difference of the frames for the fluxes in the linear response theory and in the measurement of the transport coefficients. In this connection it is worthy to mention that in linear response theory the system studied is in equilibrium: the momentum exchange with the boundaries is zero and so the barycentric reference frame is the natural choice; whereas, in laboratory experiments the boundaries of the system studied exchange momentum with the solution and this depends on the design of the experimental set up. It is the pioneering work of Schönert [3] which first delt with the problem of correlating the frames of references. He replaced the barycentric reference frame by the solvent fixed frame of reference which takes into account of the experimental boundary conditions. However, that work was also restricted to the case of binary solution, with the beauty of incorporating the concept of intra-(tracer) diffusion into the irreversible thermodynamics to regain the Kubo relations. So the work does not give directly an estimate of the velocity correlation coefficients for more general situation of (*i*) limiting diffusion of third species in a supporting electrolyte solution, (e.g. Tracer A in the solution of BC) or (*ii*) any of the ternary (mixture of two binary electrolyte having one common constituent or any electrolyte which dissociates into three different ionic species in solution. In this work we are giving an estimation of the velocity correlation coefficients for any of the aforementioned ternary systems in terms of the experimentally measurable transport coefficients. The general morphology is based on two works - one from Schönert [3] and the other from Miller [4]. Besides our attempt, the work of Raineri and Timmerman [5] also deals with the VCC's in ternary electrolytes but the equations there need to rewritten in terms of experimental quantities to be useful which is rather compicated.

Theoretical:

Our systems consists of three different solute components $i = 1,2,3$ (any one among these may be the isotope of either of the two) dissolved in

the same solvent, $i = 0$. The entropy production σ of this solution in the isothermal isobaric condition is given by

$$T\sigma = \sum_{i=0}^{3} (J_i)_w X_i \tag{1}$$

where w designates the velocity of the reference. The $(J_i)_w$ and X_i are the corresponding fluxes and forces of the ith component. For example in the solvent fixed reference frame

$$T\sigma = \sum_{i}^{3} (J_i)_0 X_i \qquad [because\ (J_0)_0 = 0] \tag{2}$$

and in the barycentric reference frame

$$T\sigma = \sum_{i=0}^{3} (J_i)_v X_i \tag{3}$$

where v is the velocity of the solvent. As the fluxes $(J_i)_o$) of the solute constituents are referred to the velocity of the solvent, the phenomenological transport equations of the irreversible thermodynamics which describe our system for a flow linear along the space co-ordinate x are

$$(J_i)_0 = \sum_{k=1}^{3} L_{ik} X_k \qquad (i = 1, 2, 3)$$

$$with \quad X_k = -\frac{\partial}{\partial x}(\mu_k + z_k F\phi)$$

or, in matrix notation,

$$\mathbf{J_0} = \mathbf{LX} \tag{4}$$

where L_{ik} are the phenomenological coefficients constituting L, μ_k are the chemical potential, z_k are the signed charge number of the constituents k, F is the Faraday constant and ϕ is the electrical potential.The phenomenological coefficients L_{ik} obey the Onsager's reciprocity relations. These coefficients can be related to the conventionally used transport coefficient:

the conductance Λ, the transferance numbers t_i and the solvent fixed thermodynamic diffusion coefficients (l_{ik}) and the volume fixed interdiffusion coefficients D_{ik}.

Now, as we consider the case from the view point of the linear response theory, the reference velocity is the velocity of the center of mass, w=v and as the total mass flow is zero

$$(J_o)_v = -\frac{1}{M_o}\sum_{i=1}^{3} M_i(J_i)_v \tag{5}$$

Again from Gibbs-Duhem equation we have

$$\sum_{i=0}^{3} C_i X_i = 0 \tag{6}$$

Now eliminating $(J_o)_v$ and (X_o) from equation (3) and we rewrite the entropy production equation in the barycentric frame as

$$T\sigma = \sum_{i=1}^{3}(J_1)_v Y_i \tag{7}$$

where $Y_i = \sum_k(\delta_{ik} + \frac{M_i C_k}{C_o M_o})X_k$ is the force conjugate to the flow $(J_i)_v$. With this the transport coefficient matrix in the barycentric reference frame comes to be,

$$\Omega = \beta^T L \beta \quad \text{(where ikth element of } \beta \text{ is } = \delta_{ik} + \frac{M_i C_k}{C_o M_o})$$

Knowing the Ω matrix, the normalised velocity correlation coefficient f_{ij} can be calculated using the relation

$$f_{ij} = \frac{N_0 V}{3}\int_0^\infty < v_{i\alpha}(0).v_{j\beta}(t) > dt = \frac{RT\Omega_{ij}}{C_i C_j} - \frac{D_i^* \delta_{ij}}{C_i}$$
$$(i,j = 0,1,2,3) \tag{8}$$

where, Ω_{ij} is the transport coefficient matrix element of ith row jth column in the barycentric reference frame, D^* is the intra(tracer)-diffusion coefficient, (here the concept of the labelled constituents has been introduced into the formalism of irreversible thermodynamics), V is volume of all the ensemble, $v_{i\alpha}$ is the velocity of αth particle of the ith species in the barycentric frame of reference, R is the universal gas constant, N_0 is the Avagadro Number.

Experimental

The ^{134}Cs (tracer) diffusion coefficient for the $CsCl$ and KCl aqueous solution have been measured in our laboratory over the concentration range 0.009 to 10.0M [6] and 0.001 to 4.0M [7] respectively. These diffusion data coupled with the other transport data existing in the literature are utilised to calculate the velocity coefficients for each system upto concentration 4.0M to the get profile of the concentration dependence of the VCCs. The diffusion coefficients are measured in our laboratory by a radioactive tracer technique utilising the sliding cell mechanism. The details are given in an earlier work [6]. The concentration dependence of the ten sets of calculated VCC for each system have been shown in fig.1 and fig.2. The curves were extended to meet the diffusion coefficient axis. Now we endeaver to interpret the trend exhibited in the concentration dependence of VCC on a microdynamical level. The velocity correlation coefficients for the ions having same type of charge ($f_{11}, f_{22}, f_{33}, f_{12}$) go through a minima as concentration of the electrolyte increases. At higher concentrations where are the fluidity is small all motional processes are damped out rapidly and so integrals over the time correlation functions will be smaller. Velocity correlation coefficients for ions having opposite types of charges f_{13}, f_{23}, have a marked assymetry in the behaviour. The most interesting is the concentration dependence of the water-water coefficient. It has the completely

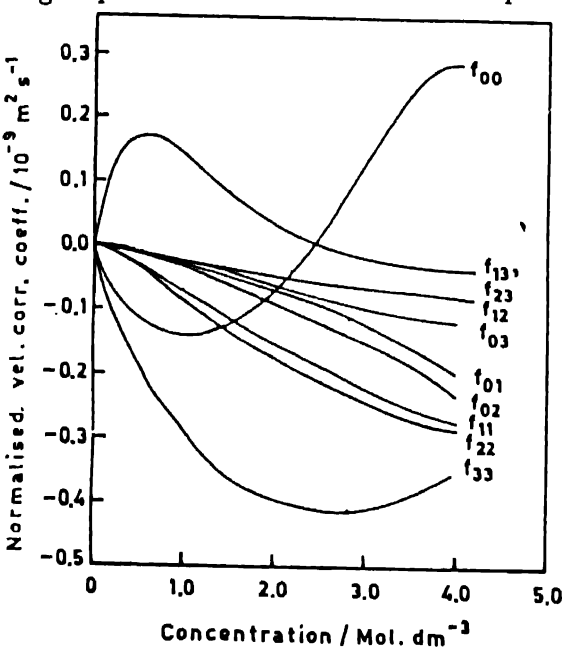

Fig.1 Concentration dependence of the velocity correlation coefficients when ^{134}Cs transporting in aqueous solution of CsCl.

opposite profile in the two systems. The experimental data is in accordance with the distorted hydrogen bond model of liquid water.

One inference can be drawn from an evaluation of the pertient experimental data is that the electrical current fluctuations in high concentrations of the electrolyte solutions considered here are such that, if an instateneous fluctuation is for instance produced by the motion of the positive charges then this fluctuation does not decay by a reversal of this positive current together with the superposition of a flow of negetive charge in the direction of original positive current fluctuation, rather, the positive current flows almost completely back.

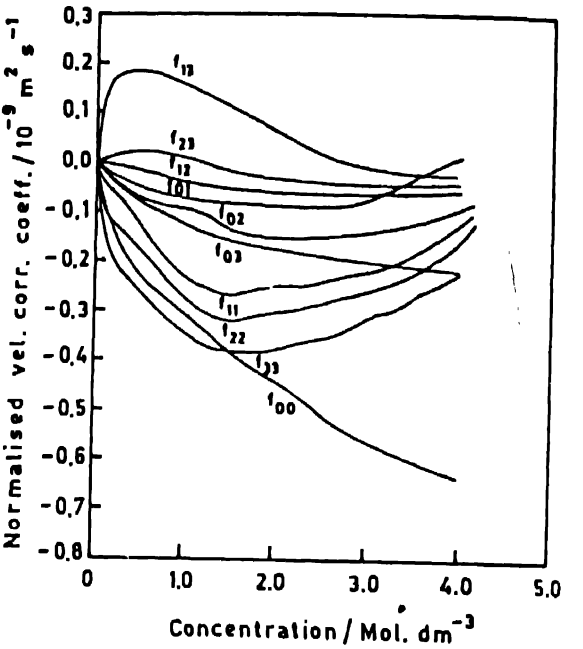

Fig.2 Concentration dependence of the velocity correlation coefficients when ^{134}Cs transporting in aqueous solution of KCl.

A detailed picture of the microscpic interactions between pairs of ions can be built up from the consideration of these velocity correlation coefficients. It can be shown also how self diffusion and conductivity behaviour of electrolyte solution would be affected by these ionic interactions. However we shall defer this more detailed analysis until a later paper.

Acknowledgement

One of the author (HC) likes to thank C.S.I.R. for financial assistance during the period of this work.

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